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A LATTICE DYNAMICAL MODEL OF THERMAL
INITIATION OF SOLID EXPLOSIVES

F. J. OWENS

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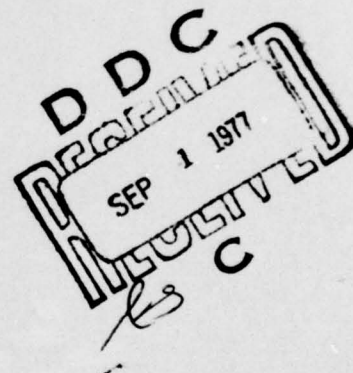AUGUST 1977

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It is proposed that the thermal initiation of a solid explosive results from a chemical reaction between the ions of the lattice induced by large amplitude vibrations of the ions at the initiation temperature. Such vibrations would allow the ions of the lattice to approach each other enabling chemical reaction to occur. The large amplitude vibrations are possible in a solid in which lattice potentials are softer and more anharmonic. Reaction rates for this mechanism are formulated in terms of the force constants

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20. ABSTRACT (Continued)

of the normal modes of vibration for the case of a simple cubic solid. Comparison of available lattice dynamical data, such as neutron diffraction and Raman studies for the isostructural pair KN_3 and TlN_3, the latter of which is unstable, support the possibility of softer and more anharmonic potentials in explosive solids.

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INTRODUCTION

The purpose of this report is to propose a microscopic model of thermal initiation of a solid explosive and to examine existing data for some simple solid explosives to test the validity of the proposal. Past efforts to understand the process in solids have involved macroscopic formulations using continuum mechanics and emphasizing processes in the detonation regime (Ref 1 and 2). However, these approaches are not fundamental in the sense that they do not view the solid as an array of quantum particles. The initiation of explosion, the process whereby a chemical reaction commences which then induces a self-sustaining series of exothermic reactions, is operative in the solid state and therefore should be influenced by the solid state properties of the material.

It will be proposed that the initial reaction in the explosive solid is caused by direct contact of adjacent anions of the solid which can arise because the modes of the explosive lattice are softer and the potentials of the lattice more anharmonic. Reaction rates for such a mechanism will be developed in terms of the force constants of the normal modes of vibration for the case of a simple cubic lattice. The resulting reaction rates will be used to examine the effect of softer and more anharmonic modes on the reaction rates. Available measurements of lattice mode frequencies in potassium azide (KN_3), a non-explosive, and the isostructural explosive thallous azide (TlN_3) will be compared to test the validity of the model. Other properties of the materials will also be considered.

THEORY

The initiating reaction in the explosion of a solid is considered to arise by the chemical interaction of two or more anions of the solid. The explosive solid then must have ions capable of interacting exothermically. The reaction is not believed to involve direct dissociation of the anion. Such a process is endothermic and of itself could not lead to detonation. The products of this decomposition could, however, react with each other exothermically. However, at 300°C (the typical initiating temperature of primary explosives) or less, it can be estimated that there would be an insufficient number of products available which would lead to a reaction with sufficient yield of energy to cause detonation. It seems more probable that the reaction is between existing ions of the lattice rather than products of the direct decomposition of the anions of the solid.

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If this is the case, the question arises as to how the ions of the lattice can get sufficiently close to undergo chemical reaction at the initiation temperature. It is proposed that the chemical contact between the ions of the lattice is induced by large amplitude vibrations of the ions at the initiation temperature. There are two aspects of the potential that influence the ions ability to make contact with the adjacent ions. If an ion at position r_0 sees a potential of the form,

$$V(r - r_0) = K(r - r_0)^2 - g(r - r_0)^3 \qquad (1)$$

the average displacement $<r - r_0>$ (not the amplitude of vibration) for the case where kT is large compared to the anharmonic term is (Ref 3)

$$<r - r_0> = (3g/4K^2)kT \qquad (2)$$

Note that the average displacement (but not the amplitude of vibration) is zero for a harmonic potential. The expression shows clearly that when g is large and K is small, the average displacement is large. Note also that small K will mean large amplitudes of vibration. Perhaps then one reason why TlN_3 is explosive and KN_3 is not is that the explosive lattice has softer, more anharmonic potentials, which serve to enhance the probability of chemical contact between the ions. Only force constants of normal modes which involve motions that allow the ions of the lattice to approach each other need be softer. A further desirable feature of the model is that in the explosive these modes would be more susceptible to softening with increasing temperature.

Relationship Between Force Constants and Reaction Rates

It is assumed when the adjacent ions in a lattice have a certain critical amplitude of vibration, A_c, the ions will be sufficiently close to chemically interact. Referring to Figure 1, consider two adjacent ions of a lattice having mass m_1 and m_2 separated by a distance, L, and vibrating in a potential $V(x)$. Only ions of potential energy $V(A_c)$ or above will be able to react. Note that the vibration of the particles must involve motions which allow the ions to approach each other. This limits the specific modes of vibration that can be

involved in the reaction. The fraction f_i of the particles in the
i th mode which have energy $V(A_c)$ or greater is

$$f_i = \exp\ (-V(A_c)/2kT) \tag{3}$$

The total number of particles in the system having amplitudes greater
than A_c is nf_i where n is the total of all particles in the system.
The particles on the average will approach each other $\tau/2$ where τ
is the period of oscillation. Thus the reaction rate, R, is

$$\frac{\omega_1}{\pi}\ n\exp\ (-V(A_c)/2kT) \tag{4}$$

It is, of course, a serious over simplification to assume that a re-
action is turned on suddenly at some precise separation or amplitude
of vibration A_c. More realistically, the reaction probability will
be a gradual function of the separation of the reacting species.
Equation 4 can be multiplied by a factor which is a function of A
and describes the probability of reaction once a given A is achieved.

Example of a Simple Cubic Lattice

The above discussion indicates how reaction rates in a solid can
depend on the force constants and frequencies of the normal modes of
vibration of the solid. In order to show the role of these modes in
the reaction process, a simple face-centered cubic explosive solid
will be considered. Such a simple structure for an explosive solid
is not unrealistic. The high temperature phase of TlN_3, from which
the material explodes, is known to be a body-centered cubic lattice,
as is ammonium nitrate (Ref 4 and 5). For purposes of illuminating
the ideas, a number of simplifications will be made in the analysis.
First, only nearest neighbor interactions in the lattice will be con-
sidered; also, the analysis will be made for zero wave vector. In
the transverse optical mode, depicted in Figure 2, the ions oscillate
parallel to Y, but the wave is propagating along X. The harmonic
force constants are defined in Figure 2. It can be shown that for
K=0, and including only nearest neighbor interactions, the frequency
is given (Ref 6) by

$$\omega = \sqrt{\frac{m_1 + m_2}{m_1 m_2}\ (2A + 4B)}. \tag{5}$$

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A similar analysis can be made for the other modes. However, when the motions of the accoustical modes are examined, it is seen that they do not allow the ions to approach each other. In this example, the reaction is considered to be between ions of mass m_1 and m_2. If the fact that the ions of the lattice are really polarizable ions is included in the analysis, the effective force constant for the transverse optical mode can be shown to be (Ref 6)

$$K_{eff} = (2A + 4B - q^2/(\frac{3v}{4\pi} - \alpha))$$ (6)

where q is the charge on the ions, V is the volume of the unit cell, and α is the polarizability of the ion. The important point is that for the t.o mode, the effect of including polarizable point charges in the analysis is to make the force constant softer. For an ionic lattice, the last term in K_{eff} can be 30% of the total force constant. Thus the polarizability of the ions plays an important role in determining the softness of a force constant, a fact which is germane to explosive solids. Combining Equations 4 and 5, a reaction rate for the probability of interaction of ions 1 and 2 in the harmonic approximation for $K_x=0$ of a face-centered cubic lattice is obtained to to be

$$R = \frac{n}{\pi} \sqrt{\frac{(m_1 + m_2)}{m_1 m_2}} \ K \exp(-KA_c^2/2kT).$$ (7)

The influence of the strength of the force constant on the reaction rate can be seen by considering a hypothetical situation.

In Figure 3, the reaction rate versus force constant is plotted for a number of different assumed values of A_c where m_1 is taken as a thallous atom and m_2 the azide ion. The result indicates that, depending on the value of A_c, the reaction rate will increase with the decreasing force constant. Interestingly the mode need not soften completely to zero for the reaction rate to reach a maximum. The maximum possible reaction rate for a given value of A_c can be obtained from Equation 7 to be

$$R_{max} = \sqrt{\frac{m_1 + m_2}{m_1 m_2}} \ (kT/A_c^2) \ e^{-1/2}$$ (8)

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If it is assumed that the maximum reaction rate is the rate necessary for explosion, the above expression indicates a relationship between the initiation temperature and the mass of the ions in the lattice.

When the above analysis is made including the anharmonic terms in the potential, the bimolecular reaction rate can be enhanced with increasing anharmonicity and decreasing force constant. Thus given two isostructural materials. EX_n which is explosive and SX_n which is stable, the lattice potential should be softer and more anharmonic in the EX_n. These differences in the potential should be reflected in a comparison of a number of basic properties of the materials, such as mode Gruneisen parameters, dielectric constants, coefficients of thermal expansion, and, of course, the mode frequencies themselves.

EXPERIMENTAL EVIDENCES FOR THE MODEL

In this section the properties of some primary explosives solids will be examined to see if there is any possible experimental support for the proposal. Although other materials will be considered, the emphasis will be on azides and fulminates because there is more available data for these materials than for other solid primary explosives, and because they are structurally simple. In particular, structural isomorphs such as TlN_3 and KN_3, have relatively simple structures and quite strikingly different stabilities. Such isomorphs allow a comparison of fundamental properties to test the ideas of the model.

Equation 8 suggests that there should be a relationship between the initiation temperature and the cation mass in a series of explosives having the same anion. The initiation temperature versus cation mass for a series of monovalent fulminates is plotted in Figure 4 and indicates a trend of the initiation temperature with cation mass. Interestingly a similar plot for the divalent azides shows a trend, but in the opposite sense. It should be emphasized that the concept of an initiation temperature is not well defined. The major difficulty is that there is a dependence on the time the material is held at a given temperature before it initiates, which is related to the geometry of the sample and the thermal conductivity as well as to the method of measurement. To minimize these problems, only initiation temperatures obtained by one method with one consistent definition were used in the plot (Ref 7).

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Despite the fact that materials of different electronic and crystal structure are being compared in Figure 4, it is remarkable that the trend exists at all. This trend may be suggestive of the role of a lattice dynamical mechanism in the initiation process.

The most direct way to test the assumptions of the model is to examine measured frequencies of lattice modes in the structurally iso-morphic explosive solids. Both TlN_3 and KN_3 have D_{4h}^{18} symmetry and a body-centered tetragonal unit cell which is shown in Figure 5 (Ref 8). In Table 1 are listed the measured K=0 mode frequencies for TlN_3 and KN_3, obtained from Raman and infrared studies (Ref 8 and 9). The data indicates that the $T(E_u)$ and $T(E_g)$ translational modes and the $R(E_g)$ librational mode of the azide ion have substantially lower frequency in the explosive solid. The motion of the individual ions associated with the modes that have lower frequency in the explosive are shown in Figure 6. It is clear that the motion of the ions for the $T(E_u)$ and the $R(E_g)$ modes involves the approach of the azide ions to each other. It is necessary to look at the data a little closer to assess whether a reduced frequency necessarily means a lower force constant. It could be simply a result of the heavier cation mass in the TlN_3. Because the force constant and the mode frequency are simply related, the $R(E_g)$ mode will be considered as an example. If mode coupling and anharmonicity are neglected, the frequency of the librational mode is given by

$$\omega^2(E_g) = \frac{2}{I}\left(\frac{\partial^2 E}{\partial\theta^2}\right)_{\theta_o} \tag{9}$$

The second derivative of the potential in the expression is the spring constant of the mode. The I is the moment of inertia of the azide ion, which is $2m\Delta^2$. The calculated force constant for the $R(E_g)$ mode of TlN_3 is 3.0×10^{-3} dyne-cm compared to 25.0×10^{-3} dyne-cm for KN_3. Thus the force constant for this mode in the explosive is about a factor of eight softer in the explosive. Modes with softer force constants will have larger amplitudes of vibration. In Table 2 are listed amplitudes of vibration of the E_g librational mode in TlN_3 and KN_3 at 293 K obtained from neutron diffraction and Raman data (Ref 8, 9, and 10). It is clearly seen that the N_3^- in TlN_3 will have a larger amplitude of libration at a given temperature than in KN_3. Of course it is the amplitude at the initiation temperature that is important. A rough estimate of the amplitude of libration at 600 K can be made from Cruickshank's formula for the case where $kT > h\nu$ (Ref 11)

$$\theta^2 = kT/4 \ \pi^2 I\nu^2 \tag{10}$$

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From available temperature-dependent measurements of the frequency of the mode, the frequency of the mode at 600 K can be obtained. The calculation leads to a librational amplitude of 26 degrees in TlN_3, compared to 8 degrees in KN_3. Thus there is a significant difference in the amplitudes of vibration for this mode between the explosive and the nonexplosive. Certainly such a large amplitude of vibration would allow adjacent azides to make a closer approach to each other at 600 K in TlN_3. The librational motion of the azide ion associated with the $R(E_g)$ mode involves an oscillation of the ion about 110 (or $1\bar{1}0$ for the other site). Such a motion would bring the end of one azide ion (which are adjacent to each other along the C axis) closer to the center of the nearest neighbor along C. Taking the covalent radii of the nitrogen as 1.5 Å and using the lattice parameters at the highest temperature of measurement (498 K), it is calculated that an angle of 48 degrees would allow the nitrogens of the azides to "touch." The force constant at the initiation temperature can be calculated from Equation 9, then used in Equation 3 to estimate the fraction of the total number of azides in the lattice that would have amplitudes large enough to allow contact. The result indicates that more than 23% of the ions of the lattice would have the necessary amplitude, a surprisingly large number.

It must be emphasized that there is no evidence to conclude that such a contact of the covalent radii as described above will induce chemical reaction between the azides. The motivation of the discussion has been to demonstrate that it is quite reasonable that a significantly large percentage of the azides can get closer in the explosive because of the softer librational mode. Certainly contact of covalent radii is not a valid criteria for inducing chemical reaction. A similar analysis for the translational mode leads to the same conclusion, that a significant number of the ions of the lattice can get closer to each other in the explosive compared to the nonexplosive. Further research is necessary to determine which of the modes is more conducive to causing reaction between the azide ions. Such an investigation would require a study of the reaction probability as a function of the different ways the two ions can approach each other.

In this discussion of the librational mode, the role of anharmonicity was ignored. If it is included, the effect could be to increase the susceptibility of the ions to get closer as previously discussed relative to Equation 2. A measure of the anharmonic term in a potential of a mode of vibration is obtained from the mode Gruneisen constant γ_j, which is obtained by pressure measurements of the mode frequencies in conjunction with a knowledge of the coefficient of thermal expansion. The γ_j has been measured for the $R(E_g)$ mode in KN_3 to be 2.04, compared to 6.5 in TlN_3, clearly indicating a larger anharmonic contribution to the a lattice potential of the explosive

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lattice (Ref 12). The Gruneisen parameters have not been reported for the translational modes in these materials. Another indicator of a higher anharmonicity in TlN_3 is the larger coefficient of thermal expansion. At a 180°C the expansion coefficient along the C axis is 17.5×10^{-5} for TlN_3 compared to 9.2×10^{-5} for KN_3 (Ref 12).

With one exception, no other solid explosive which can be thermally initiated from the solid state has been the subject of sufficient lattice dynamical studies to allow a test of the model. The one exception is a material quite different from the azides, S_4N_4. The material can be initiated at 205°C and pressure and temperature studies of the mode frequencies have been made (Ref 13). The substance has a monoclinic unit cell with four S_4N_4 molecular units per unit cell (Ref 14). The internal structure of the S_4N_4 molecule is that of a D_{2d} cradle-shaped ring. The lowest observed mode at 43 cm^{-1} (at 30 K) is a librational mode which softens by almost 50% as the initiation temperature is approached (Ref 13). The mode is also sensitive to pressure. The large amplitude associated with this libration would induce contact between two S_4N_4 units. Kemmey (Ref 15) has calculated the potential energy of the linear azide ion as a function of the displacement of the ion along its axis in $Pb(N_3)_2$. The potential of the azide ion at one site was found to be quite soft and anharmonic.

CONCLUSIONS

A mechanism of thermal initiation of a solid explosive has been considered. It is proposed that chemical reaction leading to detonation occurs because adjacent anions at the initiation temperature can make chemical contact as a result of having large amplitude vibrations. Large amplitude vibrations would result from softer modes of vibration. Only force constants of modes which allow the ions to approach need be softer. The model does explain how a large number of reactions can occur in a relatively short time. Because of the absence of experimental data, no definitive quantitative test of the model is possible at this time. However, an examination of mode frequencies in TlN_3 and KN_3 appears to support the possibility. Modes which allow the azides to approach in TlN_3 appear to be softer in the explosive. The proposal has been formulated in the simplest possible terms. A more vigorous development is not warranted at this time due to the sparcity of experimental data to test the mechanism.

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Table 1

Frequencies of lattice modes of KN_3 and TlN_3
at K 0 measured at room temperature from Raman spectroscopy

	$T(E_u)$	$T(A_{2u})$	$T(E_g)$	$R(B_{1g})$	$R(E_g)$	Ref
			cm^{-1}			
KN_3	166	80	192	159	k47	8,9
	130					
TlN_3	128	83	36	173	51	8,9
	96					

Table 2

Amplitudes of libration of the E_g mode in KN_3 and TlN_3
obtained from Raman spectroscopy and neutron diffraction

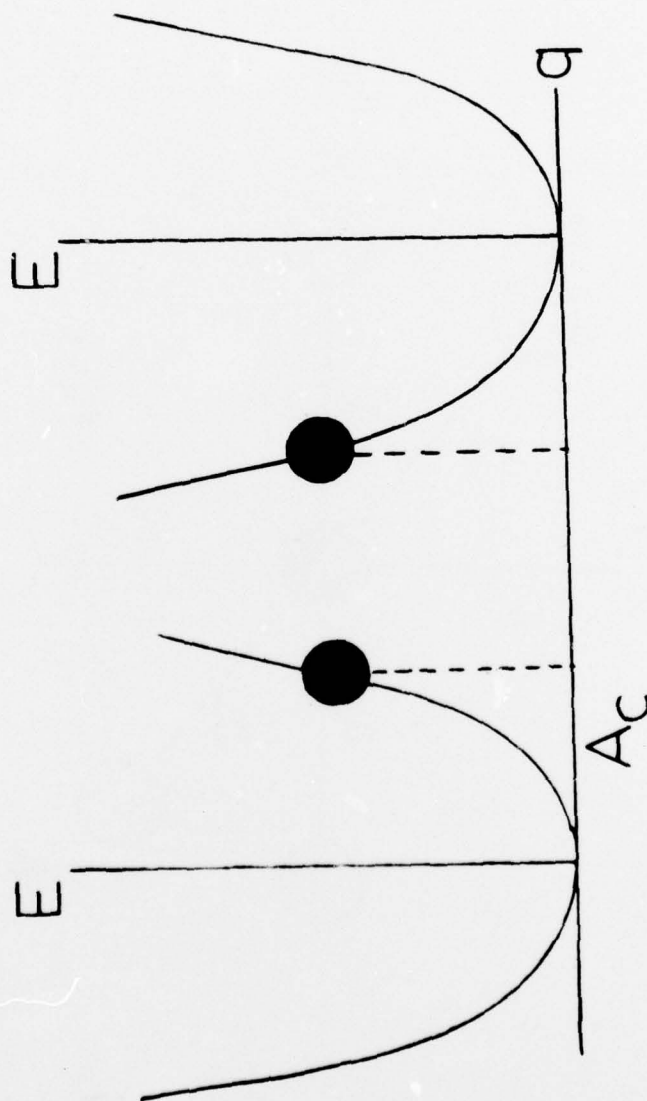|	Temperature (K)	θ (Neutron)	θ (Raman)	Ref
KN_3	293	3.51	3.15	10
TlN_3	293	9.42	14.58	10

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Fig 1   Potential energy versus separation of two
         adjacent ions in a crystal

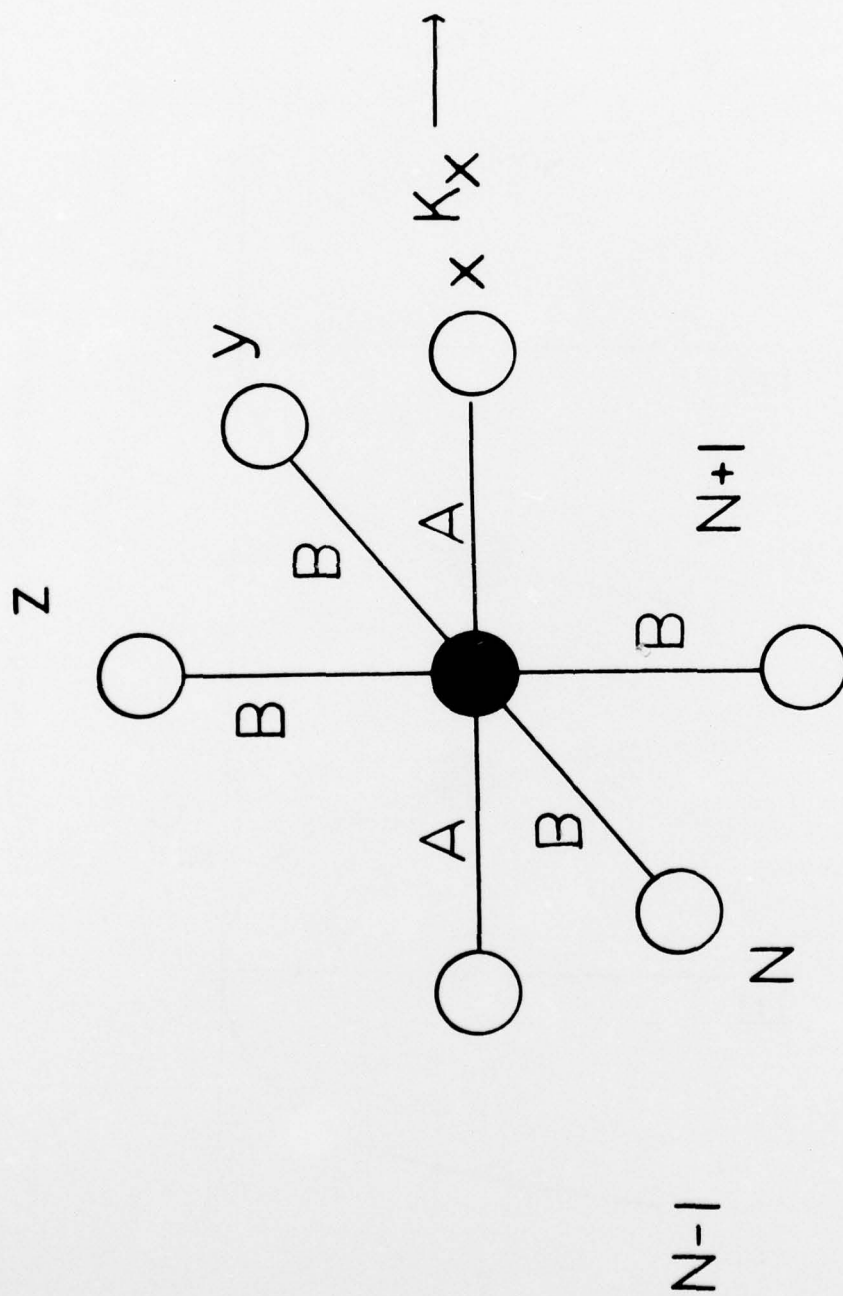13

Fig 2   Face-centered cubic lattice showing
nearest neighbor force constants

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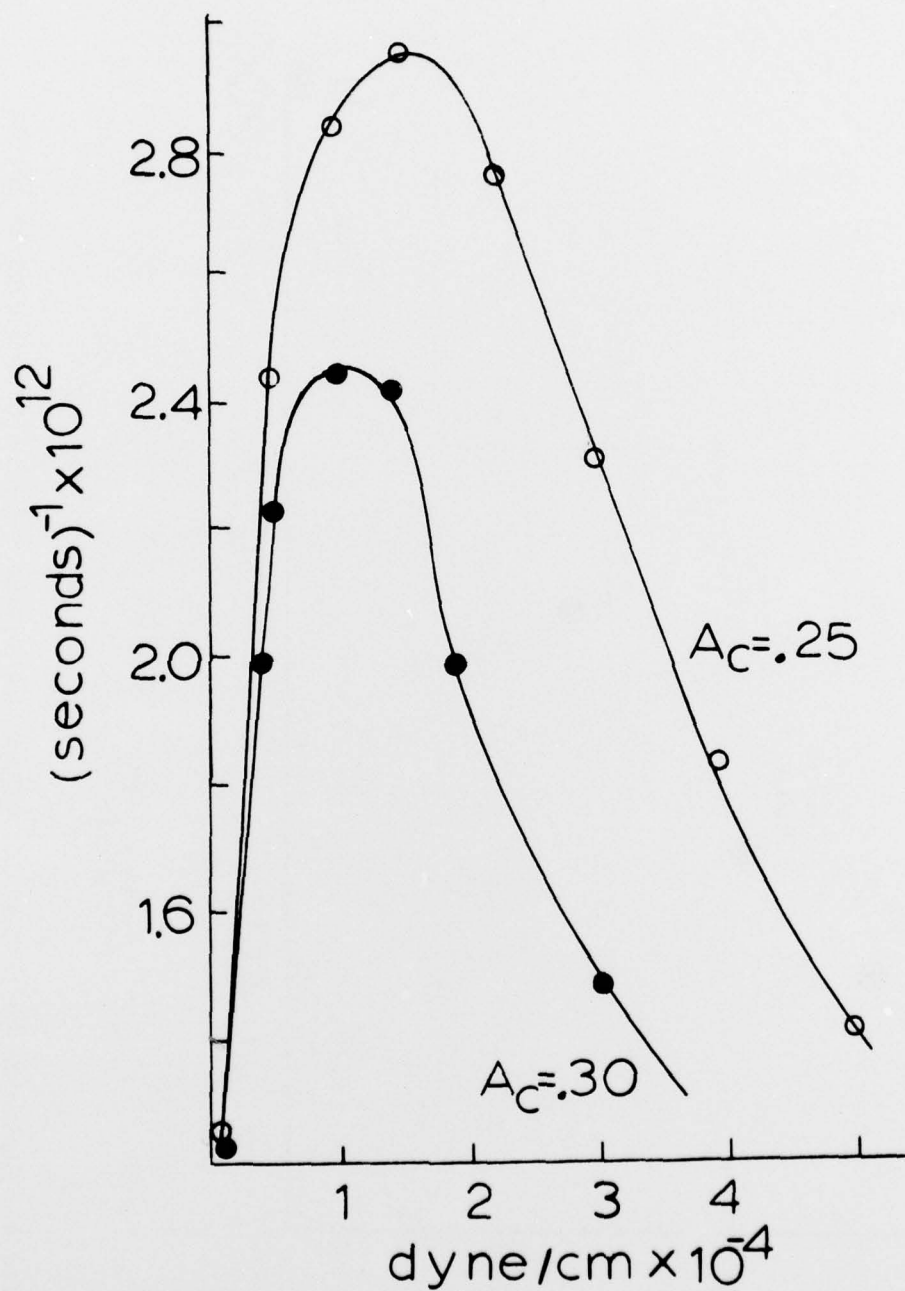
Fig 3   Reaction rates versus force constant of transverse
         optical mode in face-centered cubic lattice for
         different value of "Contact amplitude" A_c

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Fig 4   Explosive initiation to temperature versus ratio of cation mass to cation radii for a series of monovalent explosive fulminates

Fig 5   Unit cell of KN_3 and TlN_3

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Note: Modes and those which are softer in the explosive TlN$_3$.

Fig 6   Motion of ions for the K = 0, T(E$_g$), T(E$_u$), and R(E$_g$) modes in KN$_3$ and TlN$_3$

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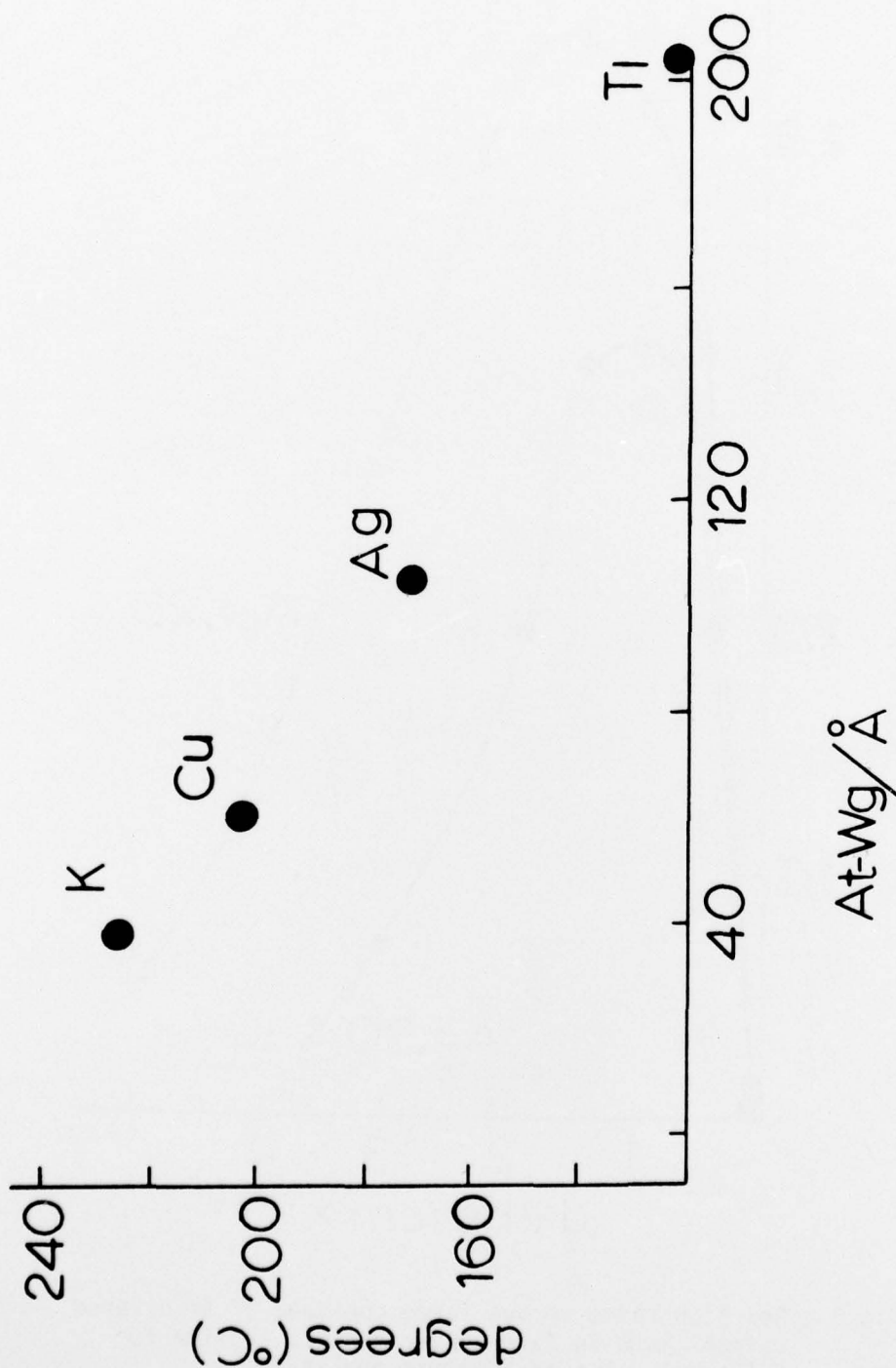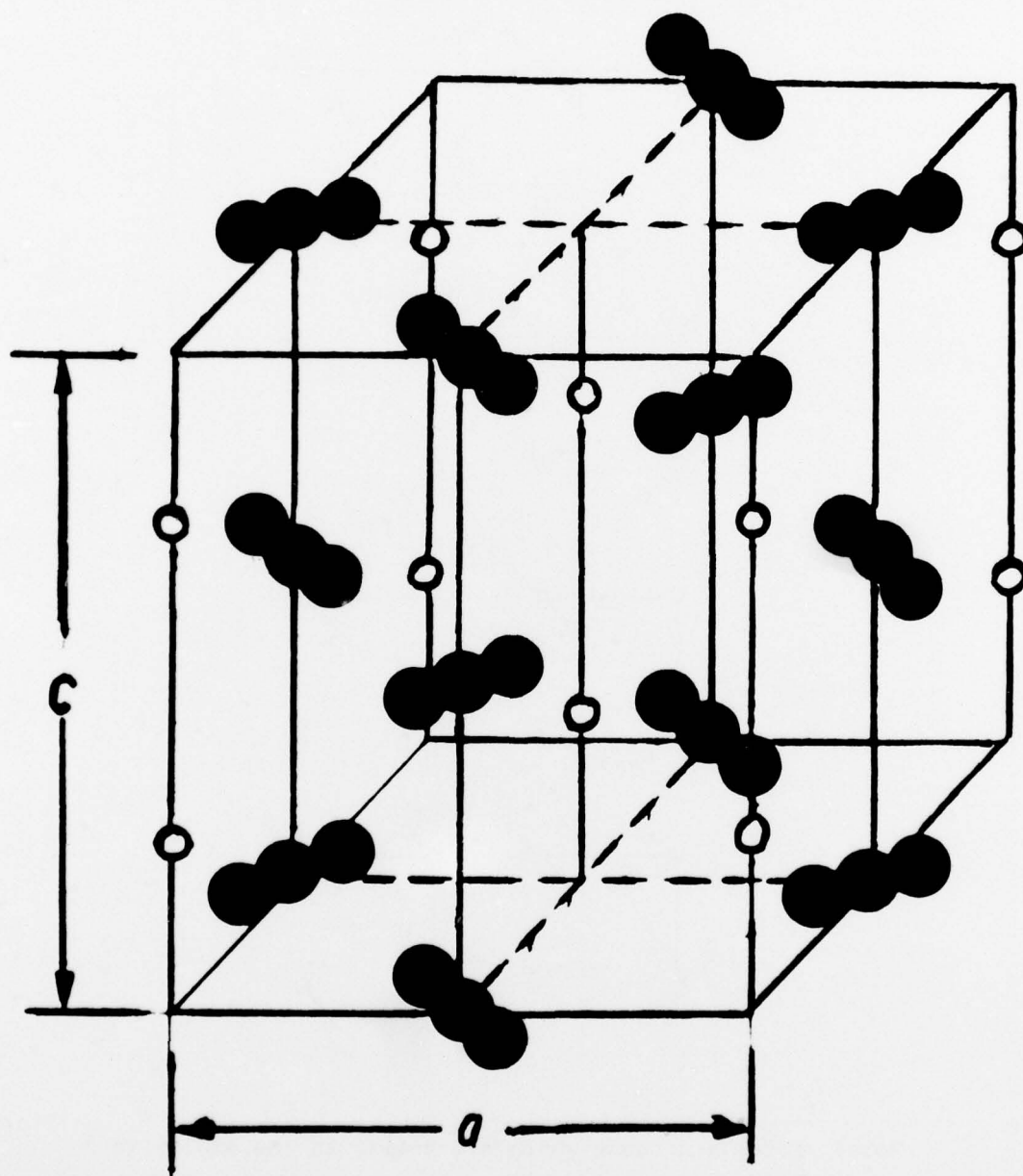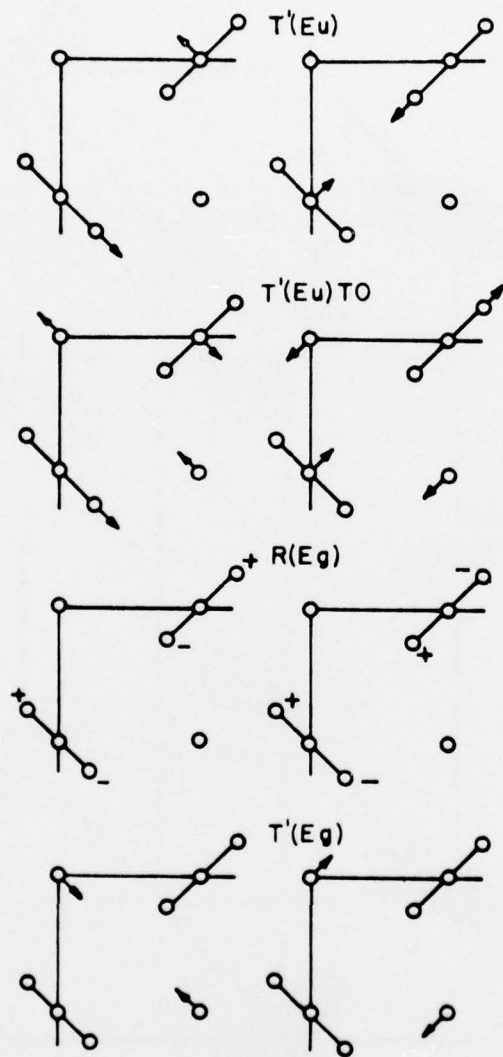
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